

LA-UR-19-29730

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Intended for: Report

Issued: 2019-10-08 (rev.1)

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September 26, 2019

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Executive Summary

In this annex to a previously reported study, a series of laboratory screening tests was conducted to identify low-temperature glasses that have significant potential for use in disposition of technetium from a Hanford Tank Waste Treatment & Immobilization Plant (WTP) secondary liquid waste stream. Specifically, a glass waste form is sought that would be suitable for on-site disposition of technetium, salts, and other species in a Tc-rich stream recovered by ion exchange from the future Effluent Management Facility (EMF) evaporator concentrate.

In the current study, several additional candidate glasses were identified, and testing of previous candidates was extended to include the Toxicity Characteristic Leaching Procedure (TCLP). In non-radioactive testing with rhenium surrogate, new formulations incorporated a simulated ion exchange eluate at temperatures below 750 °C to produce an amorphous, or mixed crystalline-amorphous, product. Incorporation of technetium (NaTcO₄)-containing simulated eluate was evaluated for two of these glasses. Technetium was not retained well in these glasses, confounding the previous conclusion that Tc volatilization during vitrification can be reduced by appropriate selection of low-temperature glasses. Preliminary data for additional low-temperature glass compositions and recommendations for future work are provided.

This report is a deliverable associated with requisition 55068-004-03 NFE-17-0020 "Candidate Low-T Glass Waste Forms for EMF Bottoms On-Site Disposition Alternative."

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Table of Contents

Executive Summary	ii
List of Acronyms and Abbreviations	iv
Introduction.....	5
Objective.....	5
Technical Approach	5
Experimental Methods.....	6
Preparation and Characterization of Glasses	6
Leaching of RCRA and Matrix Elements	7
Technetium Volatility	7
Results	8
Low-Temperature Glass Screening Tests.....	8
Tin(II) Phosphate ($\text{SnO-P}_2\text{O}_5$) Glasses	8
Vanadate (V_2O_5) Glasses	9
Tellurite (TeO_2) Glasses	11
Bismuth Borate ($\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$) Glass.....	14
Leaching of RCRA and Matrix Elements	15
Technetium Volatility During Melting	16
Summary of Findings.....	21
Literature Cited.....	23
Acknowledgements.....	24

List of Acronyms and Abbreviations

DI	Deionized
EDX	Energy-Dispersive X-ray Spectroscopy
EMF	Effluent Management Facility
EPA	Environmental Protection Agency
ICP	Inductively Coupled Plasma
LANL	Los Alamos National Laboratory
LDR	Land Disposal Requirements
LSC	Liquid Scintillation Counting
mol	Mole
MS	Mass Spectrometer/Spectrometry
MW	Molecular Weight
OES	Optical Emission Spectrometer/Spectrometry
PXRD	Powder X-ray Diffraction
RCRA	Resource Conservation and Recovery Act
SEM	Scanning Electron Microscopy
TCLP	Toxicity Characteristic Leaching Procedure
wt	Weight
WTP	Hanford Tank Waste Treatment & Immobilization Plant

Introduction

Objective

This report describes a brief set of laboratory tests to investigate low-temperature ($T < 750^{\circ}\text{C}$) glasses that have potential for use in disposition of technetium from a Hanford Tank Waste Treatment & Immobilization Plant (WTP) secondary liquid waste stream. Specifically, a glass waste form is sought that would be suitable for on-site disposition of technetium, salts, and other species in a Tc stream recovered by ion exchange from the future Effluent Management Facility (EMF) evaporator concentrate. The background and rationale for dispositioning this Tc stream in a low-temperature glass was described in more detail in a previous report by our laboratory [Tang 2018]. Following on the initial work reported in FY18, this report addresses the initial screening of new glass formulations for their melting temperatures, compliance with Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDR), and retention of pertechnetate (TcO_4^-) ion during incorporation of a simulated effluent.

Technical Approach

Prior work by Los Alamos National Laboratory (LANL) identified several low-temperature glass-making processes and glass composition types that may be satisfactory as technetium waste forms for Integrated Disposal Facility disposition [Ding 2017]. An initial test series using cold and radioactive waste simulants validated the concept that selected low-temperature glasses can improve retention of technetium during vitrification of a Hanford secondary waste stream. The Tc volatility experiments identified three instances of vitrification at $\leq 700^{\circ}\text{C}$ in which $\sim 90\%$ or more of the technetium was successfully retained for one hour in the melt. These glasses were fabricated from oxides of Pb-B, Te-Pb, and Bi-B-Ba. However, these glasses all contain bulk elements that are regulated under the Land Disposal Restrictions (LDR) of the Resource Conservation and Recovery Act (RCRA). In the current study, glass formulations that do not include RCRA-regulated elements were especially of interest.

Candidate glass families evaluated in this study included tin(II) phosphates ($\text{SnO}_2\text{-P}_2\text{O}_5$), vanadate (V_2O_5) and tellurite (TeO_2) glasses, in addition to a bismuth borate glass carried forward from previous work. To accomplish these goals, the following series of experiments was performed. Due to the limited scope and duration of this project, some testing could not be performed on all candidate formulations.

Low-temperature glass composition tests: Candidate glass formulations from the literature were prepared in crucibles in furnaces to validate that their melting temperatures were $\leq 750^{\circ}\text{C}$, with and without addition of a simulant containing NaReO_4^- (surrogate for NaTcO_4^-) and representative concentrations of alkali metal salts. Design of the rhenium-containing “cold” simulant is described in the previous report [Tang 2018] and its composition is given in Table 1. The samples were determined to be amorphous and/or crystalline using powder x-ray diffraction (PXRD), and their homogeneity was determined by scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDX) mapping. Retention of rhenium in the melt was qualitatively verified in the EDX spectra.

Leaching of RCRA and matrix elements: To determine whether the waste-loaded glass compositions are potentially LDR compliant, samples of non-radioactive glass were leached according to the Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP) [EPA Method 1311]. Leaching data on additional elements was also evaluated for information on glass durability trends.

Retention of technetium during melting: For two of the new glasses, a small-scale test was conducted to determine the fraction of technetium released from the melt during glass formation and simulated waste incorporation. Design of the technetium-containing simulant is described in the previous report [Tang 2018] and its composition is given in Table 2.

Experimental Methods

Preparation and Characterization of Glasses

Non-radioactive glass samples were prepared using commercial reagent-grade chemicals (e.g. oxides, fluorides), typically of $\geq 99\%$ purity on a metals basis, in accordance with the methods described in the previous study [Tang 2018]. For the technetium retention experiments, a NaTcO_4 solution (0.247 mol/L) was prepared in DI water, and added to the glass as a separate aliquot to provide 45.9 mg of NaTcO_4 per

Table 1. Cold simulant formulation with NaReO_4 .

Additive	MW	mol/L in concentrate	mg salt/mL solution
NaReO_4	273	8.28E-02	22.6
NaOH	40	1.50E-01	6.00
Na_2CO_3	106	1.00E-01	10.6
KNO_2	85	4.80E-02	4.08
NaNO_3	85	3.45E-02	2.93
K_2SO_4	174	6.49E-03	1.13
K_2CrO_4	194	5.00E-04	0.097

Table 2. Simulants for technetium experiments. Separate aliquots of NaTcO_4 solution (1 mL) and cold salts (1 mL) were added and mixed with the glass-forming oxides.

Additive	MW	mol/L in concentrate	mg salt/mL solution
"Hot" Solution			
NaTcO_4	186	2.47E-01	45.9
"Cold" Solution			
NaOH	40	1.50E-01	6.00
Na_2CO_3	106	1.00E-01	10.6
KNO_2	85	4.80E-02	4.08
NaNO_3	85	3.45E-02	2.93
K_2SO_4	174	6.49E-03	1.13
K_2CrO_4	194	5.00E-04	0.097

1 g of glass. The other salts were prepared as a cold simulant in a similar manner as above (Table 2), and 1 mL of this simulant was added to each 1 g of glass. This provided an additional 24.8 mg of salt, for a total salt addition of 7 wt%.

Leaching of RCRA and Matrix Elements

Glass samples were size-reduced to pass through a 9.5 mm (0.375 inch) standard sieve. Analysis methods followed the Toxicity Characteristic Leaching Procedure with the following variances. Sample size for determining the extraction solution was 1 g, instead of the recommended 5 g. Glasses were tested in duplicate, with sample size for extraction was ~2 g and test solution added at the prescribed 20:1 ratio. All of the glasses required test solution “A”.

A volume of 10 mL of filtered leachate was treated with 0.3 mL of concentrated HNO_3 and heated to reduce the volume and remove acetic acid from the sample matrix for analysis. This step was repeated several times until the solution turned colorless. The final solution was quantitatively transferred to a test tube and diluted with 2% HNO_3 to a 10 mL volume. On several samples, a second 10-mL aliquot was spiked with a known amount of the specified elements (matrix spikes), to verify recovery. In addition, a process blank was prepared with each batch and carried through the entire sample preparation process.

The solutions were analyzed directly using a Thermo Scientific iCAP inductively-coupled plasma optical emission spectrometer (ICP-OES) and a Thermo Scientific X-Series inductively-coupled plasma mass spectrometer (ICP-MS). Sample dilutions were made as necessary so the concentration of the analytes remained inside the linear range of the calibration curve. The ICP-OES is calibrated daily with National Institute of Standards and Technology traceable multi-element standards. Calibration standards and calibration blanks were run before and after the samples, serving as quality control measures in addition to the preparation blank and matrix spike. Acceptance criteria are detailed in the LANL analytical chemistry procedure for TCLP [ANC134].

Technetium Volatility

Glass precursor powders were accurately dispensed to within 0.001 g of the amount required to prepare 1.000 g of each targeted glass composition. After ball-milling, the 1-gram portion of precursor powder was transferred to a glass vial. Using a paper funnel, the oxide mixture was spread along an alumina boat ($\sim 6 \times 1 \times 1$ cm). The glass vial was rinsed with 1 mL of sodium pertechnetate solution (0.229 mmol, 45.1 mg) and 1 mL of cold simulant solution, and then this 2 mL rinse was added dropwise to the boat to allow the oxides to absorb it. The boat was placed in a quartz tube assembly designed for heating the sample under a slow flow of air (50-100 mL/min). Solv-seal joints (Andrews Glass) were used to connect the gas inlets and outlets, and the air flow terminated in a water bubbler. Details of this apparatus have been published [Childs 2015, Tang 2018].

The sample was heated at 5 °C/min in a clamshell furnace to 110 °C, where it was allowed to dry for one hour. Water droplets condensed outside the heated portion of the tube during this operation. Then the sample was further heated to the melting (flowability) temperature of the glass over the course of 1 hour (equivalent to approximately 10 °C/min), then held at this temperature for 1 hour under the slow flow of air. After cooling to room temperature, the condensed water was removed from the quartz tube using glass wool, and the boat was removed by pulling it from the left (upstream) side with a wire hook.

The quartz tube and glass wool were rinsed with a portion of DI water sufficient to remove all solid residue, by visual inspection, and to provide a solution concentration suitable for UV-vis measurement. The inner surface of the tube was swabbed with a moistened laboratory wipe, which was surveyed to verify that negligible (<1000 counts per minute) removable Tc activity remained.

Based on intensities of absorption at 287 nm ($\epsilon = 2170 \text{ M}^{-1}\text{cm}^{-1}$) [Schwochau 2000] in the UV-visible spectra of the water washes, the TcO_4^- in each solution was quantified. Absorption spectra were recorded on a Cary-50 spectrometer between 200 and 800 nm in a 1-cm quartz cuvette. DI water was used as a baseline. The glass wool plug was similarly washed with water and the TcO_4^- concentration (C_1) in the total rinse volume (V_1) was quantified using the Beer-Lambert Law. After the concentration was determined, the equivalent mass (m_1) of NaTcO_4 (molecular weight 186 g/mol) recovered was calculated using the equation $m_1 = 186 \cdot C_1 V_1$. The fraction of Tc that was volatilized and recovered (%) was calculated using $(m_1 \cdot 100)/m_0$, where m_0 is the initial mass of NaTcO_4 introduced in the glass.

Technetium-99 in the water wash solutions was quantified by liquid scintillation counting. Standards and samples were prepared by mixing 10 mL of Ultima Gold AB scintillation cocktail and 10 mL of aqueous $^{99}\text{TcO}_4$ solution, prepared by DI water dilution of a 10 μL aliquot of the wash solution or standard. Each sample was counted for 10 min on a Perkin Elmer Tri-Carb 3100TR. A calibration curve was prepared using three dilutions of the same NaTcO_4 stock solution (0.229 mmol/mL) that was used in preparing the glass samples. Molar concentrations (M_1) of ^{99}Tc in the aliquots were calculated using the empirical linear fit to the calibration curve, and this result was scaled to the total wash solution volume, i.e. $\text{mol}_1 = M_1 \cdot V_1$. Then the fraction of Tc that was volatilized and recovered (%) was calculated using $(\text{mol}_1 \cdot 100)/\text{mol}_0$, where mol_0 is the initial moles of NaTcO_4 introduced in the glass.

Results

Low-Temperature Glass Screening Tests

The glass viscosity and melting temperature range for each glass was evaluated based on visual observation. The furnace temperature was raised in increments of 50 °C and then held, and melting temperature of each glass was qualitatively assessed when the liquid could be moved easily around the crucible and poured from the container for quenching. Glasses were quenched in air on a stainless steel pan after melting, except as noted, and the presence of amorphous and/or crystalline phases was determined by PXRD. The melting temperature range and PXRD results of candidate glass formulations are summarized in Table 3. Based on these experimental results, most of the candidate glasses met the melting temperature requirement for further evaluation ($T \leq 750 \text{ }^\circ\text{C}$).

Tin(II) Phosphate ($\text{SnO-P}_2\text{O}_5$) Glasses

Two glass formulations based on Sn(II) oxide and P_2O_5 were newly examined. Binary oxide $60\text{SnO} \cdot 40\text{P}_2\text{O}_5$ [Morinaga 2001] melted and became pourable at 650-700 °C, while no melting was observed for the calcium-containing composition $50\text{SnO} \cdot 33\text{P}_2\text{O}_5 \cdot 17\text{CaO}$ [Hong 2010] at temperatures up to 800 °C. Incorporation of the rhenium-containing simulant into $60\text{SnO} \cdot 40\text{P}_2\text{O}_5$ was attempted, but a vigorous exothermic reaction occurred during ball-milling. Figure 1 shows the residue of this reaction. Similar

Table 3. Summary of melting study on candidate glass formulations, with cold simulant incorporated. All compositions are reported on a mol% basis.

Glass Family	Batch Composition (Mol%)	Melting Point (°C)	PXRD
SnO-P ₂ O ₅	60SnO·40P ₂ O ₅	650-700	reaction
	50SnO·33P ₂ O ₅ ·17CaO	>800	--
V ₂ O ₅	50V ₂ O ₅ ·50TeO ₂	550-600	amorphous
	53V ₂ O ₅ ·4ZnO·22.4BaO·20.6P ₂ O ₅	600-650	amorphous
TeO ₂	47.5TeO ₂ ·47.5MoO ₃ ·5Bi ₂ O ₃	550-600	amorphous
	78TeO ₂ ·12WO ₃ ·10Bi ₂ O ₃	575-625	--
	40TeO ₂ ·40B ₂ O ₃ ·20Bi ₂ O ₃	650-700	mixed
	78TeO ₂ ·22PbO	600-650	amorphous
Bi ₂ O ₃ -B ₂ O ₃	65Bi ₂ O ₃ ·20B ₂ O ₃ ·15BaO	650-700	mixed



Figure 1. Photograph of residue from exothermic reaction of 60SnO-40P₂O₅ glass with simulant during ball milling.

reactivity was observed in the prior study when Sn(II) fluorophosphate glass precursors were mixed with the cold simulant. This result indicates that the solid-phase reaction of stannous ion with oxidizers such as nitrate or perrhenate is the source of the exotherm. While it might be advantageous to stabilize pertechnetate by incorporating it into a reducing melt, further laboratory experimentation on ball-milled samples containing Sn(II) precursors is not advised.

Vanadate (V₂O₅) Glasses

Glasses containing vanadium oxides were not examined in the previous study of low-temperature vitrification for technetium. Two candidates were identified for this study, based on the binary V₂O₅-TeO₂ system [Dimitriev 1978, Kaur 2018] and the ternary or quaternary V₂O₅-BaO-P₂O₅ systems [Vedeanu 2012, Naito 2011]. It is important to note that although vanadium is not regulated under the RCRA hazardous waste standard, its leachability is regulated to 1.6 mg/L TCLP under the land disposal restrictions standard applicable to onsite disposal of such a waste form [40 CFR 268]. Thus, while these glasses are emerging as lead-free alternatives for electronics applications, their use in the vitrification application requires the same deliberation as lead- or barium-containing glasses.

A vanadium tellurite glass, 50V₂O₅-50TeO₂, melted below 600 °C as its base composition and after addition of the rhenium-containing simulated eluate. The appearance of both glasses was intensely

brown-black in color, and nearly opaque (Figure 2). The powder x-ray diffraction pattern for both glasses indicated that the structure was amorphous (Figure 3). The two-humped amorphous feature in these and other PXRD patterns is a frequent characteristic of the low-melting glasses, and has been reported in bulk metallic glasses, polymers, and ceramic composites [Warren 1990; Egami 2003]. The first hump is characteristic of the short-range disorder of the amorphous material, and the second hump at higher scattering vector value is related to the medium-range disorder/ The SEM image of simulant-loaded $50\text{V}_2\text{O}_5\text{-}50\text{TeO}_2$ shows a homogeneous glass phase (Figure 4). In the EDX spectrum, the dominant peaks are V, Te, and O from the base glass composition, and Na and Re peaks are also observed. The small Al peak is assumed to come from dissolution or adhesion of the alumina crucible; this feature is commonly observed in the spectra of the low-temperature glasses.

A second vanadate glass, $53\text{V}_2\text{O}_5\cdot 4\text{ZnO}\cdot 22.4\text{BaO}\cdot 20.6\text{P}_2\text{O}_5$, was also found to incorporate the rhenium-containing simulant at a melting temperature of 600-650 °C. Like the binary V-Te-O glass, its color was intensely brown-black and its PXRD pattern showed amorphous character (Figure 5). Since 80% of its composition consists of elements that are subject to LDR regulation (V, Zn, and Ba), it was deemed a lower priority for continued study.



Figure 2. Photographs of $50\text{V}_2\text{O}_5\text{-}50\text{TeO}_2$ glasses prepared without (left) and with (right) cold simulant, after quenching at room temperature.

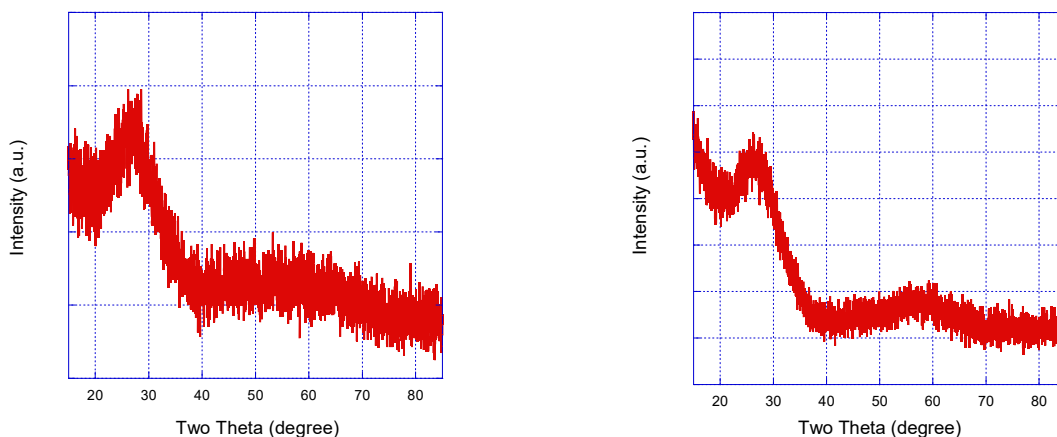


Figure 3. PXRD of $50\text{V}_2\text{O}_5\text{-}50\text{TeO}_2$ glasses without (left) and with (right) cold simulant.

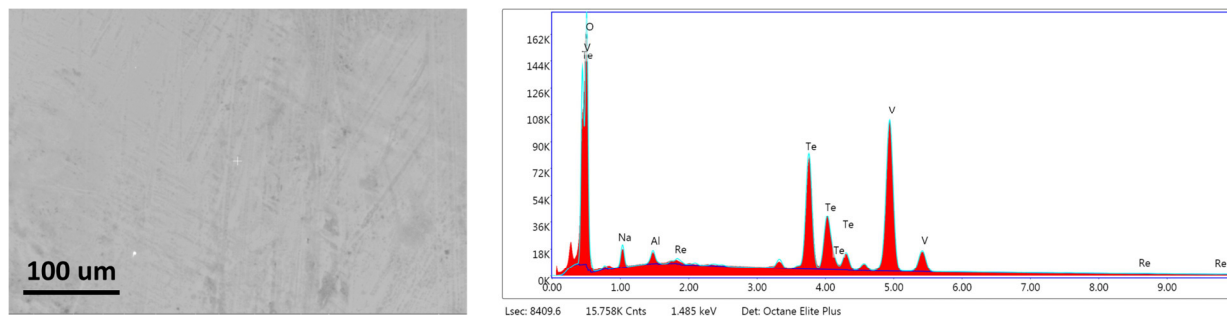


Figure 4. SEM image and EDX spectrum of $50\text{V}_2\text{O}_5\text{-}50\text{TeO}_2$ glass prepared with cold simulant.

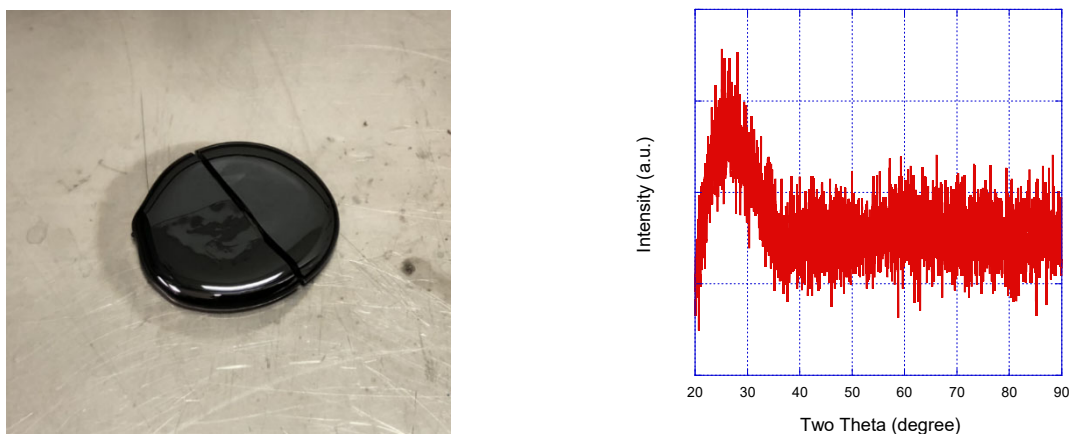


Figure 5. Photograph (left) and PXRD (right) of $53\text{V}_2\text{O}_5\text{-}4\text{ZnO}\text{-}22.4\text{BaO}\text{-}20.6\text{P}_2\text{O}_5$ glass with simulant incorporated.

Tellurite (TeO_2) Glasses

As an element that is not RCRA-regulated, tellurium-based glasses offer a wide variety of low-melting compositions that may be especially suitable as waste forms for a relatively low-volume effluent. A lead tellurite glass, $78\text{TeO}_2\text{-}22\text{PbO}$, was found to have excellent Tc retention and promising durability in our previous work. Three additional compositions have been considered in the current study: $47.5\text{TeO}_2\text{-}47.5\text{MoO}_3\text{-}5\text{Bi}_2\text{O}_3$ [Zamyatin 2016], $78\text{TeO}_2\text{-}12\text{WO}_3\text{-}10\text{Bi}_2\text{O}_3$ [Champarnaud-Mesjafw 1998], and $40\text{TeO}_2\text{-}40\text{B}_2\text{O}_3\text{-}20\text{Bi}_2\text{O}_3$ [Gupta 2017].

The Te-Mo-Bi-O glass melted and became pourable between 550-600 °C. After quenching, the base glass and the simulant-loaded glass were transparent and amber in color (Figure 6), and the PXRD showed that simulant incorporation yielded an amorphous product (Figure 7). The SEM image of simulant-loaded $47.5\text{TeO}_2\text{-}47.5\text{MoO}_3\text{-}5\text{Bi}_2\text{O}_3$ shows a homogeneous glass phase (Figure 8), and in the EDX spectrum, the dominant peaks are Te, Mo, Bi and O from the base glass composition. Na and Re peaks are also observed, along with the small Al peak from the crucible.

A tungsten-containing glass, $78\text{TeO}_2\text{-}12\text{WO}_3\text{-}10\text{Bi}_2\text{O}_3$ was also synthesized, with a slightly higher melting temperature. Its appearance was amber but opaque, suggesting a significant amount of crystallinity.

Since its composition contains relatively more tellurium and its opaque visual appearance is indicative of the presence of crystalline phases, it was deemed a lower priority for continued study than the molybdenum glass.

The other tellurite glass that was examined was $40\text{TeO}_2\cdot 40\text{B}_2\text{O}_3\cdot 20\text{Bi}_2\text{O}_3$, which melted between 650-700 °C when rhenium-containing simulant was incorporated. While the base formulation is transparent, glassy and nearly colorless, the addition of simulant produced a glass with visually distinctive regions of translucent green and opaque off-white colors (Figure 10). Powder XRD of a representative sample showed a mixture of amorphous and crystalline product (Figure 11). While it is difficult to assign the peaks in a mixed-phase material, the diffraction angles tentatively identify that 4 or 5 crystalline phases are present, including TeO_2 , B_2O_3 and ReO_3 , and Bi and Na-rich phases. The SEM-EDX shows phase inhomogeneity, and the presence of all expected elements was verified (Figure 12).



Figure 6. Photographs of $47.5\text{TeO}_2\text{-}47.5\text{MoO}_3\text{-}5\text{Bi}_2\text{O}_3$ glass prepared without (left) and with (right) cold simulant, after quenching at room temperature.

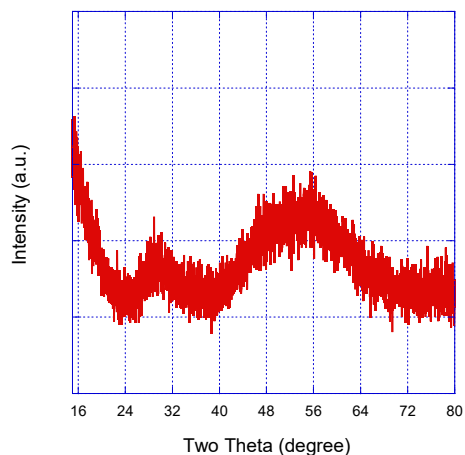


Figure 7. PXRD of simulant-containing $47.5\text{TeO}_2\text{-}47.5\text{MoO}_3\text{-}5\text{Bi}_2\text{O}_3$ glass.

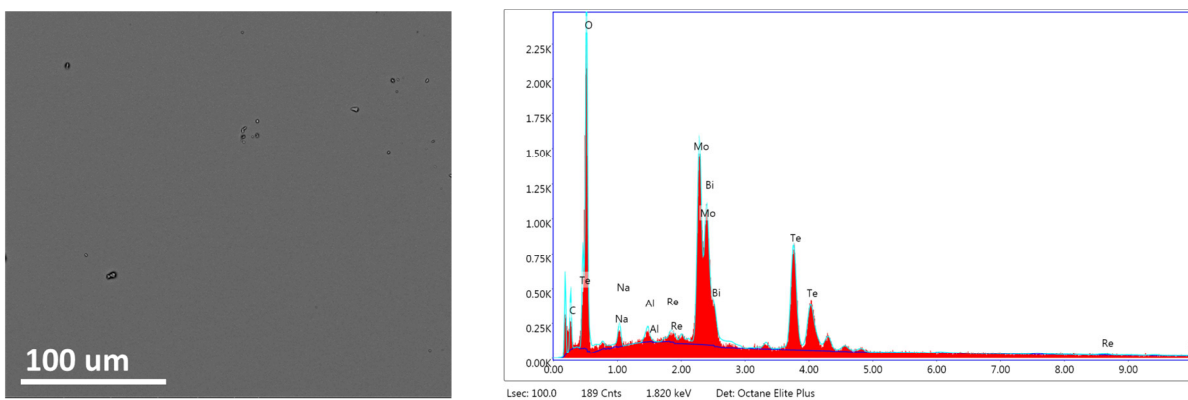


Figure 8. SEM image and EDX spectrum of 47.5TeO_2 - 47.5MoO_3 - $5\text{Bi}_2\text{O}_3$ glass prepared with cold simulant.



Figure 9. Photograph of 78TeO_2 - 12WO_3 - $10\text{Bi}_2\text{O}_3$ glass, after quenching at room temperature.

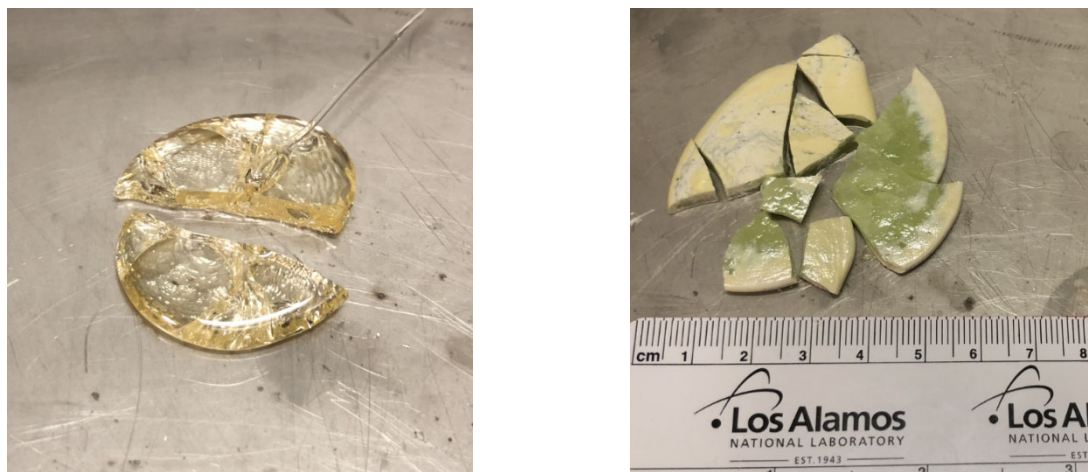


Figure 10. Photographs of 40TeO_2 - $40\text{B}_2\text{O}_3$ - $20\text{Bi}_2\text{O}_3$ glass prepared without (left) and with (right) cold simulant, after quenching at room temperature.

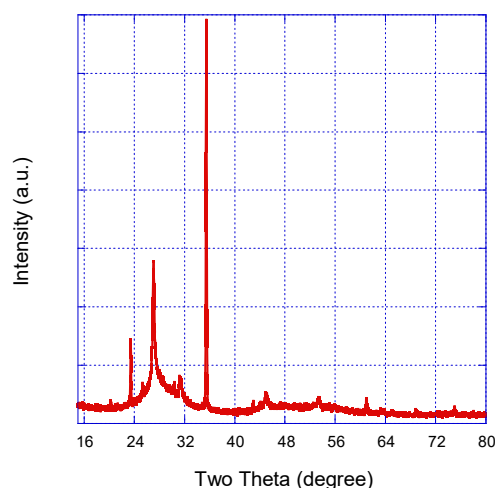


Figure 11. PXRD of simulant-containing $40\text{TeO}_2\cdot 40\text{B}_2\text{O}_3\cdot 20\text{Bi}_2\text{O}_3$ glass. The glass contains both amorphous and crystalline phases.

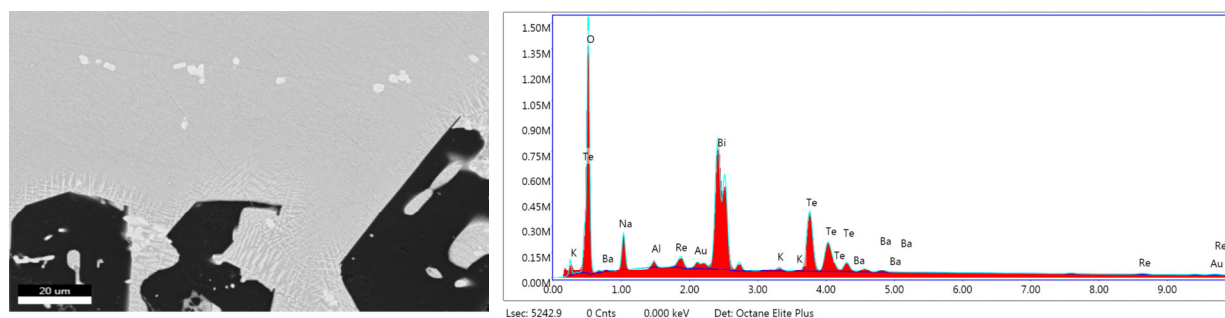


Figure 12. SEM image in cross-section (scale is $20\ \mu\text{m}$) and EDX spectrum of $40\text{TeO}_2\cdot 40\text{B}_2\text{O}_3\cdot 20\text{Bi}_2\text{O}_3$ glass prepared with cold simulant.

Bismuth Borate ($\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$) Glass

In the previous report, the bismuth borate formulation $65\text{Bi}_2\text{O}_3\text{-}20\text{B}_2\text{O}_3\text{-}15\text{BaO}$ was found to have a low melting temperature and good retention of technetium during vitrification. The crystallinity of the product was variable, however: in a larger-scale preparation with the cold simulant, the product contained both amorphous and crystalline regions with strong elemental segregation. In the 1-g scale technetium volatility experiment, the product was completely amorphous by PXRD. The ostensible difference between these two preparations was their rate of cooling: the larger sample had been quenched to room temperature on a metal plate, while the smaller sample was allowed to cool more slowly in an open clamshell furnace. For the current study, a larger-scale sample was prepared at the same melting temperature, then allowed to cool to room temperature slowly, while held in a crucible in an open muffle furnace. This third sample was highly crystalline and opaque, with no transparent glassy regions that were visually apparent (Figure 13). Once removed from the crucible, this product was observed to be more friable than the other glasses.



Figure 13. Three samples of $65\text{Bi}_2\text{O}_3\text{-}20\text{B}_2\text{O}_3\text{-}15\text{BaO}$ glass prepared at different quantities and with different cooling schemes.

Leaching of RCRA and Matrix Elements

An additional goal of this screening study was to determine the potential of the low-temperature glasses to meet RCRA LDR non-wastewater standard applicable to onsite disposal of the technetium-containing waste form. In the previous report, the three glasses with highest Tc retention during vitrification all contained lead or barium as bulk constituents. Of these, $65\text{PbO}\cdot 35\text{B}_2\text{O}_3$ was found to absorb water and leach Pb very rapidly, and it has been eliminated from further consideration. The other two, $78\text{TeO}_2\cdot 22\text{PbO}$ and $65\text{Bi}_2\text{O}_3\cdot 20\text{B}_2\text{O}_3\cdot 15\text{BaO}$, showed fair or good retention of RCRA elements in preliminary studies. In addition to these two glasses, three new formulations were subjected to Toxicity Characteristic Leaching Procedure, EPA method 1311. While some of the new base glass formulations do not contain RCRA elements, chromium as CrO_4^{2-} can be a component of EMF concentrates and is a component of the waste simulant in this study.

Glasses prepared with cold simulant were size-reduced (<9.5 mm) and tested using the EPA 1311 method, at small scale. Elements of RCRA LDR concern (Ba, V, Pb, and Cr), plus bulk constituents (Bi, B, Mo, K, Te), were analyzed in the TCLP leachate by inductively-coupled plasma mass spectrometry (ICP-MS) and optical emission spectroscopy (ICP-OES). Table 4 provides a summary of these results in the standard TCLP unit of mg/L element concentration in the leachate. For the glass matrix elements, Table 5 presents the same results in terms of the mass fraction of the original glass sample that dissolved during the leaching procedure.

Barium and boron leached extensively from the $65\text{Bi}_2\text{O}_3\cdot 20\text{B}_2\text{O}_3\cdot 15\text{BaO}$, but not congruently with the bismuth in the sample. The barium leaching was in 20-fold excess of the RCRA LDR limit. This result was significantly in excess of that predicted from the prior year study, and may be related to the slower cooling method. While it may be possible to create a more durable form of this material through suitable cooling or post-treatment, the highly variable outcome for this composition suggests that it is unlikely to become a reliable waste form. The other glass with high leachability of a non-RCRA element was $40\text{TeO}_2\cdot 40\text{B}_2\text{O}_3\cdot 20\text{Bi}_2\text{O}_3$, which lost boron at a rate incongruent with its high retention of tellurium. Like the bismuth borate material, this glass also showed significant crystallinity in its PXRD pattern. For these two glasses, a quantitative chromium value was not determined using a more concentrated

solution, because large amounts of boron will typically adhere to the ICP-MS sample introduction system and contaminate many subsequent samples.

The three other glasses were significantly more resistant to the TCLP leaching conditions. Leaching of lead from $78\text{TeO}_2 \cdot 22\text{PbO}$ was somewhat in excess of the LDR limit (3.0 versus $0.75 \mu\text{g/L}$ TCLP), and similarly, leaching of vanadium from $50\text{V}_2\text{O}_5 \cdot 50\text{TeO}_2$ was somewhat in excess of the LDR limit (7.7 versus $1.6 \mu\text{g/L}$). Other glass matrix elements such as Bi, Mo and Te, and simulant components potassium and chromium, were not significantly leached from these two glasses, nor from $47.5\text{TeO}_2 \cdot 47.5\text{MoO}_3 \cdot 5\text{Bi}_2\text{O}_3$.

Technetium Volatility During Melting

Two of the new waste-loaded glass formulations with melting temperatures below 750°C , $47.5\text{TeO}_2 \cdot 47.5\text{MoO}_3 \cdot 5\text{Bi}_2\text{O}_3$ and $50\text{V}_2\text{O}_5 \cdot 50\text{TeO}_2$, were prepared using the NaTcO_4 -containing simulant, in order to measure the release of volatile technetium during low-temperature vitrification. These glasses were selected based on their high durability in the TCLP study. The volatility experiments were performed at a 1-gram scale in the clamshell furnace apparatus described in our previous report [Tang 2018]. The simulated TcO_4^- effluent was blended and dried with the solid oxide powders, and then the sample was heated gradually to a hold temperature above the previously-determined melting point of the glass (650°C). During the heating process, volatile species were swept out of the heated zone and into the cooler portion of the quartz tube with a slow stream of air (Figure 14). These solids were washed from the tube and assayed by UV-visible spectroscopy.

The formation and release of volatile technetium during the heating could be observed as red-brown solids deposited downstream in the cool portion of the tube for both glasses. In the $47.5\text{TeO}_2 \cdot 47.5\text{MoO}_3 \cdot 5\text{Bi}_2\text{O}_3$ vitrification experiment (Figure 15), the red deposit was observed to form after the glass had been maintained at its peak temperature and was beginning to cool (Figure 16). In the $50\text{V}_2\text{O}_5 \cdot 50\text{TeO}_2$ vitrification experiment (Figure 17), the red deposit began to appear during the ramp-up to melting temperature, near 370°C (Figure 18). This latter behavior more closely resembles the volatilization of Tc from $91\text{TeO}_2 \cdot 9\text{P}_2\text{O}_5$, which occurred at approximately 300°C . These deposits may be compared to the slight amount of white solid that was deposited in the prior-year study of $78\text{TeO}_2 \cdot 22\text{PbO}$, which retained nearly all of its pertechnetate in the FY18 study.

The solids were easily washed from the tube and glass wool plug using water, and assayed for TcO_4^- by UV-visible spectrophotometry. Although the appearance of the Tc species deposited in the tube varied across different compositions and melting temperatures, there was no visual evidence of residues remaining adhered to the tube, and a final smear of the inner surface with a wet laboratory wipe verified that negligible removable ^{99}Tc activity remained in the tube.

From the solution TcO_4^- concentrations, the amount of NaTcO_4 lost to volatility was calculated. For $47.5\text{TeO}_2 \cdot 47.5\text{MoO}_3 \cdot 5\text{Bi}_2\text{O}_3$, the entire amount (100%) of TcO_4^- in the simulant was recovered from the red-brown deposit in the tube; thus, the technetium was apparently completely volatilized during vitrification. The result for the $50\text{V}_2\text{O}_5 \cdot 50\text{TeO}_2$ glass was more problematic, because the UV-visible spectrometry result indicated that 122% of the original TcO_4^- had been recovered from downstream solid deposits.

Table 4. Toxicity Characteristic Leaching Procedure (TCLP) results for RCRA LDR elements in the simulant-loaded glasses. Several other non-RCRA elements of interest are also reported. All glasses were prepared to 5% simulant loading.

Glass Sample	Key RCRA LDR Elements (mg/L)				Other elements of interest (mg/L)				
	Barium (Ba)	Lead (Pb)	Vanadium (V)	Chromium (Cr)	Boron (B)	Bismuth (Bi)	Molybdenum (Mo)	Tellurium (Te)	Potassium (K)
65Bi ₂ O ₃ :20B ₂ O ₃ :15BaO	470			n.m.	107	4.5			n.m.
78TeO ₂ :22PbO		3.0		< .002				7.8	0.86
50V ₂ O ₅ :50TeO ₂			7.7	< .002				8.0	0.61
47.5TeO ₂ :47.5MoO ₃ :5Bi ₂ O ₃				0.004		0.25	3.1	2.2	0.73
40TeO ₂ :40B ₂ O ₃ :20Bi ₂ O ₃				n.m.	360	4.0		0.05	n.m.
LDR limit (mg/L TCLP)	21	0.75	1.6	0.60					

n.m. = not measured; the element was not detectable at high dilution, and the leachate was not run at low dilution due to the large amounts of boron and/or barium in these samples.

Table 5. Elemental mass fraction (%) leached from each glass. Leaching solution was TCLP Extraction Fluid #1 at pH 4.9.

	B %	Ba %	Bi %	Pb %	Mo %	Te %	V %
65Bi ₂ O ₃ :20B ₂ O ₃ :15BaO	17.5	16.2	0.01				
78TeO ₂ :22PbO				0.02		0.03	
50V ₂ O ₅ :50TeO ₂						0.04	0.05
47.5TeO ₂ :47.5MoO ₃ :5Bi ₂ O ₃			<0.01		0.02	0.01	
40TeO ₂ :40B ₂ O ₃ :20Bi ₂ O ₃	16.0		0.02			<0.01	

Closer examination of the quartz tube in the 50V₂O₅:50TeO₂ experiment revealed that two distinct rings of solid has been deposited: a red-brown ring similar to that observed in previous Tc volatility experiments [Childs 2015, Tang 2018], and a brown-black ring that more closely resembled the color of the 50V₂O₅:50TeO₂ glass and the deposits on the exterior of the alumina crucible (Figure 18). We hypothesize that a vanadium oxide species became volatile during the experiment, since solution measurements of VO²⁺ ion show an intense absorption at 275 nm which cannot be distinguished from the peak at 286 nm for TcO₄⁻ [Brooker 2015].

To fully characterize the deposited material in these experiments would require elemental analysis, e.g. by ICP-MS, which was not available for ⁹⁹Tc containing solutions during the study period. However, it was possible to quantify the ⁹⁹Tc content in the water rinse solutions by liquid scintillation counting (LSC; Table 6). By this measurement, it was determined that 81% of the ⁹⁹Tc had volatilized from the TeO₂-MoO₃-Bi₂O₃ glass during melting, while 100% of the ⁹⁹Tc was volatilized from the 50V₂O₅:50TeO₂. These results, which are lower than the corresponding values obtained by UV-vis, suggest that *both* of the new glasses released a matrix element at their melting temperatures.

Table 6. Fraction of initial ⁹⁹TcO₄ volatilized and recovered in vitrification experiments. Quantification is by liquid scintillation counting.

Glass	% TcO ₄ recovery (LSC)
TeO ₂ -MoO ₃ -Bi ₂ O ₃	81%
V ₂ O ₅ -TeO ₂	100%



Figure 14. Apparatus for technetium volatility experiments. The glass sample was heated in an alumina boat at the center of the furnace, while a flow of air passed over it from left to right. In the cool zone to the right of the furnace, deposits of ⁹⁹Tc were formed on the tube and in a plug of glass wool.

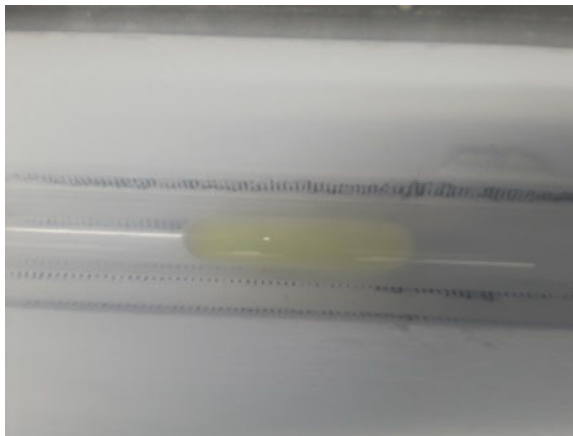
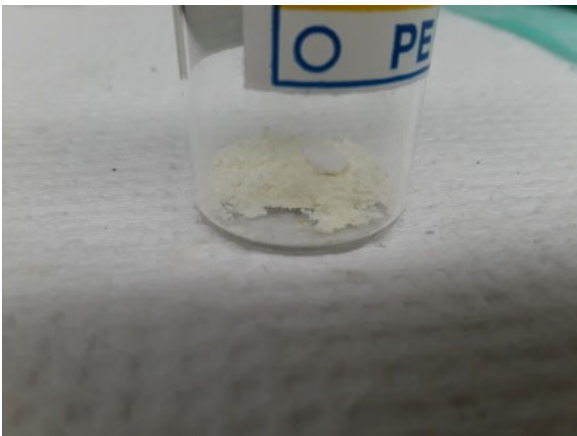


Figure 15. Mixture of tellurium, molybdenum and bismuth oxides (left). The mixture was loaded into an alumina boat, treated with a simulant containing NaTcO_4^- , and placed in a clamshell furnace (right).

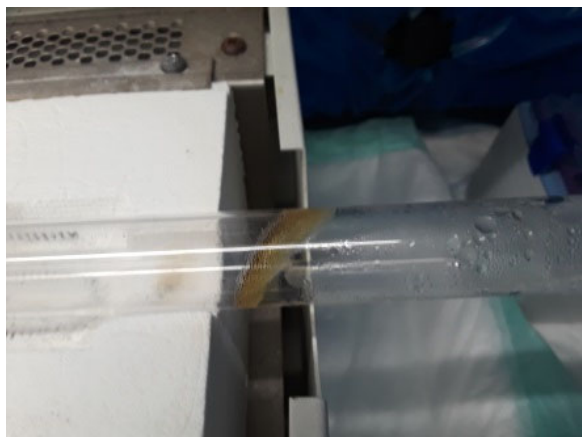


Figure 16. After heating $47.5\text{TeO}_2 \cdot 47.5\text{MoO}_3 \cdot 5\text{Bi}_2\text{O}_3$ at 650°C for 1 hour, a red-brown solid deposited on the walls of the tube (right). The glass is amber-colored at room temperature (right).

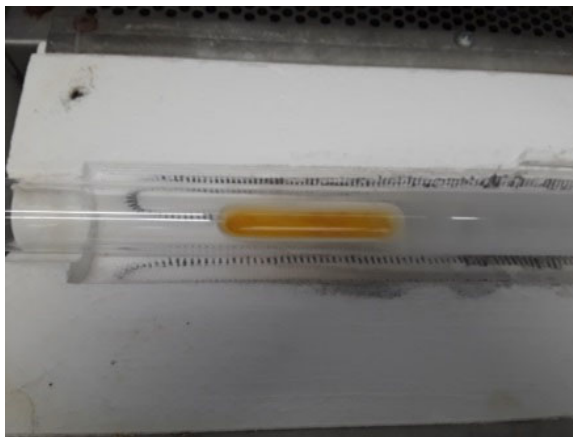
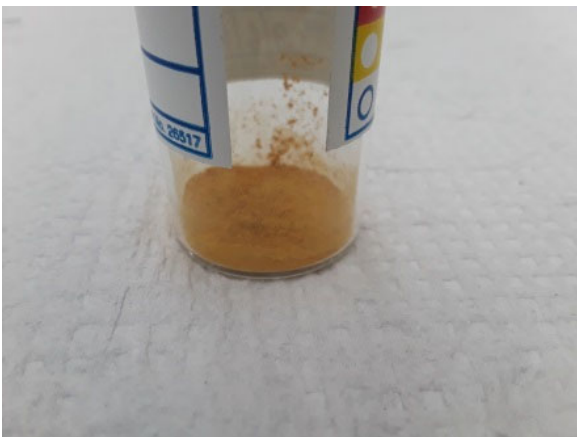


Figure 17. Mixture of vanadium and tellurium oxides (left). The mixture was loaded into an alumina boat, treated with a simulant containing NaTcO_4^- , and placed in a clamshell furnace (right).

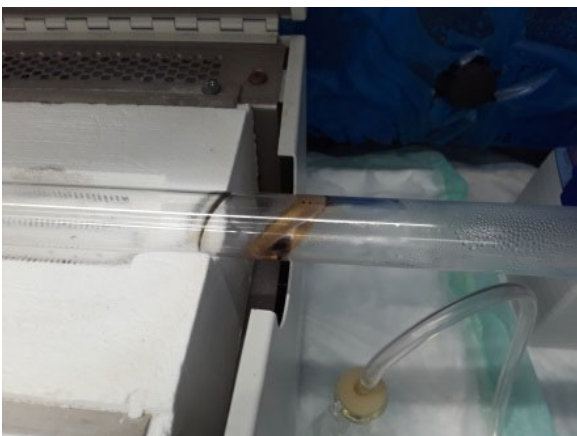


Figure 18. After heating $50\text{V}_2\text{O}_5:50\text{TeO}_2$ at 650° for 1 hour, rings of brown-black and red-brown solids deposited on the walls of the tube (right). The vanadium glass at room temperature is brown-black (right).

Summary of Findings

The cumulative results of FY18 and FY19 screening studies are summarized in Figure 19 and Table 7. While the previous screening study validated the proposal that low-temperature glasses have potential application for improved retention of technetium during vitrification of a Hanford secondary waste stream, the additional screening studies in this report reveal challenges in predicting this behavior. The newly-examined glasses, $47.5\text{TeO}_2\cdot 47.5\text{MoO}_3\cdot 5\text{Bi}_2\text{O}_3$ and $50\text{V}_2\text{O}_5\cdot 50\text{TeO}_2$, both melt below 650°C but also readily volatilize TcO_4^- and/or matrix elements. The release of 81% of the TcO_4^- from $47.5\text{TeO}_2\cdot 47.5\text{MoO}_3\cdot 5\text{Bi}_2\text{O}_3$ and 100% of the TcO_4^- from $50\text{V}_2\text{O}_5\cdot 50\text{TeO}_2$ puts these glasses in the same category of performance as $91\text{TeO}_2\cdot 9\text{P}_2\text{O}_5$, which was studied in FY18. The high losses of Tc from these glasses indicates that chemical interactions affect the Tc release, perhaps as much as temperature.

The durability of the glasses also varies. In general, the presence of crystalline phases after melting and quenching has been predictive of poor durability and high leaching of RCRA elements. However, some borate glasses that appeared amorphous by PXRD have also been very susceptible to water dissolution, most notably $65\text{PbO}\cdot 35\text{B}_2\text{O}_3$. In the current work, $78\text{TeO}_2\cdot 22\text{PbO}$, $47.5\text{TeO}_2\cdot 47.5\text{MoO}_3\cdot 5\text{Bi}_2\text{O}_3$ and $50\text{V}_2\text{O}_5\cdot 50\text{TeO}_2$ showed the highest durability in TCLP conditions. With some adjustment to the protocols for its fabrication, it may be possible for the Te-Pb-O glass to meet both the Tc volatility objective and the regulatory requirements, but replication and extension of these initial screening studies is certainly needed. For all candidate low-temperature glasses, operational criteria such as cost, waste loading, and long-term durability must also eventually be defined and evaluated.

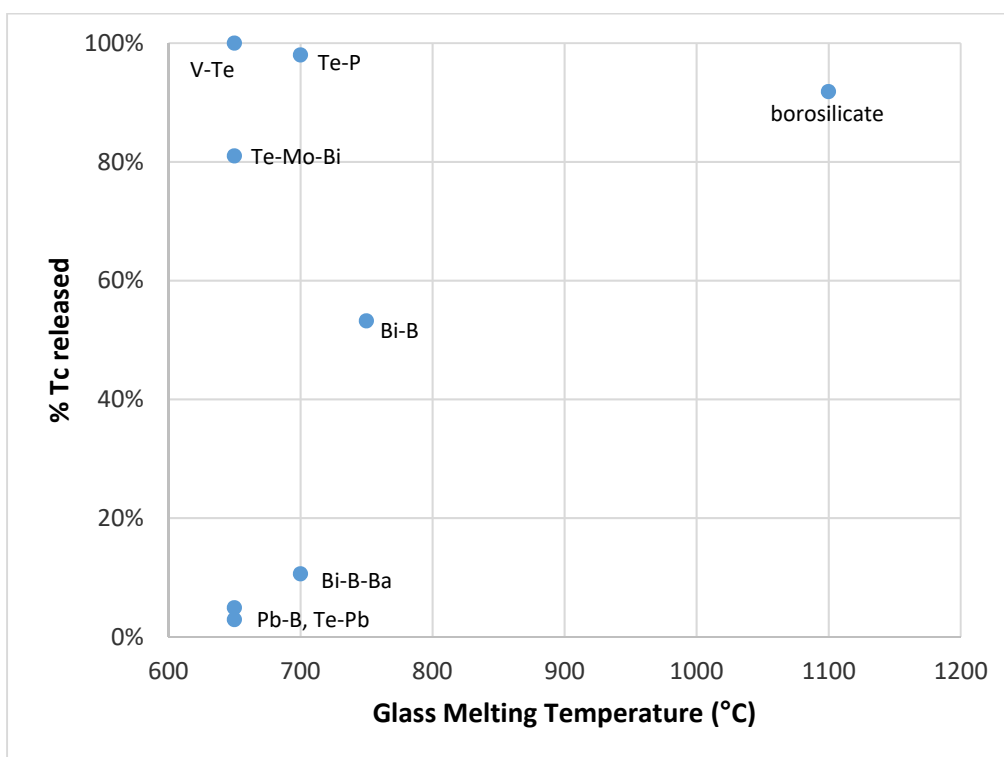


Figure 19. Summary of technetium volatility experiments. Each data point is based on recovery of TcO_4^- solids in a single furnace run.

Table 7. Summary of screening results of low-temperature glasses for Tc disposition. Glasses with new FY19 data are placed in the upper portion of the table, and blanks indicate that a property has not been measured yet. Some entries are based on the previous study [Tang 2018].

Glass Sample	Melting Temp (°C)	Glass Product	Tc Retention	LDR Compliance/Durability
78TeO ₂ ·22PbO	600-650	Yes (amorphous)	High	Possible/High
50V ₂ O ₅ ·50TeO ₂	550-600	Yes (amorphous)	Low	Possible/High
47.5TeO ₂ ·47.5MoO ₃ ·5Bi ₂ O ₃	550-600	Yes (amorphous)	Low	Yes/High
65Bi ₂ O ₃ ·20B ₂ O ₃ ·15BaO	650-700	Yes (mixed)	High	No/Low
40TeO ₂ ·40B ₂ O ₃ ·20Bi ₂ O ₃	650-700	Yes (amorphous)		Yes/Low
53V ₂ O ₅ ·4ZnO·22.4BaO·20.6P ₂ O ₅	600-650	Yes (amorphous)		
78TeO ₂ ·12WO ₃ ·10Bi ₂ O ₃	575-625	Yes (mixed)		
65PbO·35B ₂ O ₃	600-650	Yes (amorphous)	High	No/Low
91TeO ₂ ·9P ₂ O ₅	650-700	Yes (Re lost)	Low	Yes/unknown
55Bi ₂ O ₃ ·45B ₂ O ₃	700-750	Yes (amorphous)	Moderate	Yes/Low

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Acknowledgements

The authors are grateful to Dave Swanberg and Ridha Mabrouki at Washington River Protection Solutions, LLC, Richland, Washington, for funding and programmatic guidance. We also acknowledge Ning Xu and Michael Rearick in the Actinide Analytical Chemistry Group at LANL for experimental support. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC for the Department of Energy/National Nuclear Security Administration.